



Effect of mixing method on the properties of composite cathodes for all-solid-state lithium batteries using Li_2S – P_2S_5 solid electrolytes



Junghoon Kim^a, Minyong Eom^b, Sungwoo Noh^b, Dongwook Shin^{a,*}

^a Division of Materials Science & Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea

^b Department of Fuel Cells and Hydrogen Technology, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea

HIGHLIGHTS

- Composite cathodes are prepared by three different mixing methods.
- Morphological and electrochemical properties differ according to the mixing method.
- Sonication followed by wet-mixing was effective to improve the cell performance.
- Mixing method is critical for all-solid-state batteries to achieve high performance.

ARTICLE INFO

Article history:

Received 18 September 2012

Received in revised form

13 November 2012

Accepted 16 November 2012

Available online 23 November 2012

Keywords:

All-solid-state lithium ion battery

Solid electrolyte

Composite cathodes

Mixing method

ABSTRACT

Composite cathodes comprising the solid powders of LiCoO_2 , electrolyte and Super P carbon are prepared using three different mixing methods to apply to all-solid-state lithium batteries, and their morphological and electrochemical properties are compared. By applying the wet-mixing method, composite cathodes with greater homogenous distribution of solid particles are obtained when compared to those prepared by dry-mixing. As a result of this favorable feature, a higher discharge capacity of 84 mAh g^{-1} and a capacity retention of 73% are maintained at the 50th cycle in the all-solid-state cell using the composite cathode prepared by wet-mixing with a ball mixer, which resulted from the smaller interfacial resistance for the intercalation/deintercalation of the Li ions in this composite cathode. This is determined to be due to the homogenous distribution of the constituent particles leading to significantly reduced electrode polarization.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical systems with high energy and power density require continuous improvement of the safety and durability characteristics related to the use of combustible organic liquid electrolytes. This promotes the need for “all-solid-state” lithium ion batteries using non-flammable solid electrolytes. Several types of solid electrolytes based on the sulfides system have been developed to attain practically useful conductivity through numerous studies aiming at fast ionic conduction. In particular, Hayashi et al. reported that Li_2S – P_2S_5 systems have a good electrochemical stability up to 10 V combined with high ionic conductivity of $\sim 10^{-3} \text{ S cm}^{-1}$ and reasonably high cell performance [1,2]. The lithium ionic conductivity of solid electrolytes has consistently improved, and Kamaya

et al. reported recently that a new lithium superionic conductor belonging to a new structure type, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), shows extremely high ionic conductivity of $10^{-2} \text{ S cm}^{-1}$ at 27°C , which is comparable to currently used organic liquid electrolytes [3,4].

It is important to use solid electrolytes with high lithium ionic conductivity for developing all-solid-state cells with high energy and power density. In cells using organic liquid electrolytes, effective electrode (solid)–electrolyte (liquid) interfaces are easily formed by immersing the electrodes in liquid electrolytes, while in the all-solid state cells, the continuous lithium ion and electron conducting paths must be purposely formed between the solid–solid interfaces by preparing the composite cathodes containing the solid electrolyte powders mixed with the active materials and conductive additives due to little fluidity of the solid electrolyte powders. Therefore, no matter how high the ionic conductivity of the solid electrolytes becomes, designing composite cathodes with a favorable contact situation between the solid electrolyte particles and the other constituent particles is also important to fully utilize

* Corresponding author. Tel.: +82 2 2220 0503; fax: +82 2 2220 4011.

E-mail address: dwshin@hanyang.ac.kr (D. Shin).

the high conductivity of the solid electrolytes. It also has increasing influence on the high performance of the all-solid-state cell. Therefore, an effective method for preparing composite electrodes can greatly improve the electrochemical performance of the all-solid-state lithium ion batteries.

In a large number of articles on all-solid-state lithium ion batteries using sulfide based solid electrolytes, composite cathodes were prepared by dry mixing using agate mortar and pestle [5–7]. However, it is very difficult to control the particle distribution by dry mixing without the inclusion of any liquid while grinding the mixture for composite cathodes that consist of only the active material, solid electrolytes and conductive additive powders as it commonly results in the non-uniform distribution and agglomeration of the constituent particles.

Therefore, in the present work, an attempt is made to improve the performance of all-solid-state lithium batteries by modifying the mixing method for preparing the composite cathode. The effect of this mixing method on the microstructure and properties of the resulting composite cathode is also discussed in terms of the cycle performance, cell resistance and electrode polarization.

2. Experimental

The $78\text{Li}_2\text{S} \cdot 22\text{P}_2\text{S}_5$ glass-ceramic was prepared using a process modified from the previously reported high-energy mechanical milling process and subsequent heat-treatment [8,9]. Reagent-grade Li_2S (99.9%, Alfa) and P_2S_5 (99%, Aldrich) were used as starting materials. These materials were mixed thoroughly in the appropriate molar ratios, and then mechanical milling was performed at 520 rpm for 25 h using a high energy planetary ball mill (Pulverisette 7, Fritsch) with milling cycles of 40 min and rests for 20 min. The glass-ceramic was prepared from the prepared glass using a two-step heat treatment that included nucleation at 160°C and crystal growth at 230°C with ionic conductivity of $8.5 \times 10^{-4} \text{ S cm}^{-1}$.

The composite cathodes were prepared by using three types of powders: LiCoO_2 , the glass-ceramic electrolyte and Super P carbon, with weight ratios of 39:59:2. The mixing method used to prepare the composite cathodes was based on the three methods given in

Fig. 1. For method 1, all the source powders were thoroughly dry-mixed with hands using agate mortar and pestle. In method 2, prior to the mixing process, all the source materials were sonicated in toluene (1/8 in a weight ratio) as the solvent as it is stable against sulfide-based solid electrolytes. The moisture content of solvent was below 0.05%. The slurry was then evaporated to retain the minimum amount of solvent required to make the particles flow during the mixing process. This was done because the particles in the prepared slurry without any dispersants or binders are severely segregated by virtue of the differences in the size, density, shape and other properties of the particles of which they are composed. The resulting slurry was then thoroughly wet-mixed with hands, using agate mortar and pestle, which was subsequently completely dried at 130°C . Method 3 was the same as method 2 but the apparatus used for wet-mixing was switched from mortar to a ball mixer rotating at high speed. The microstructures of the composite electrodes prepared by these methods were examined to identify the change in morphologies and the distribution state of the constituent particles using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX) for determining the elemental distribution.

Electrochemical tests were performed by constructing laboratory-scaled all-solid-state cells. The composite cathode (25 mg) and the glass-ceramic solid electrolyte (140 mg) were uniaxially pressed into a disk with a diameter of 16 mm at 4 metric tons together. An indium foil (Alfa-Aesar, $t = 0.1 \text{ mm}$) as the counter electrode with an electrode potential of 0.62 V vs. Li^+/Li was then attached to the solid electrolyte surface by pressing with a pressure of 2 metric tons. After releasing the pressure, the three-layered pellets were assembled with 2032-type coin cells. All the cells were galvanostatically charged and discharged using a charge–discharge measurement device (TOSCAT-3100, Toyo system) at room temperature. The charge–discharge performance was evaluated under a constant current density of 0.06 mA cm^{-2} and cut off voltages of 1.9 and 3.6 V. The electrochemical impedance spectroscopy measurements of the obtained cells were performed using an impedance analyzer (Solartron 1260) after charging it to 3.6 V at 0.06 mA cm^{-2} .

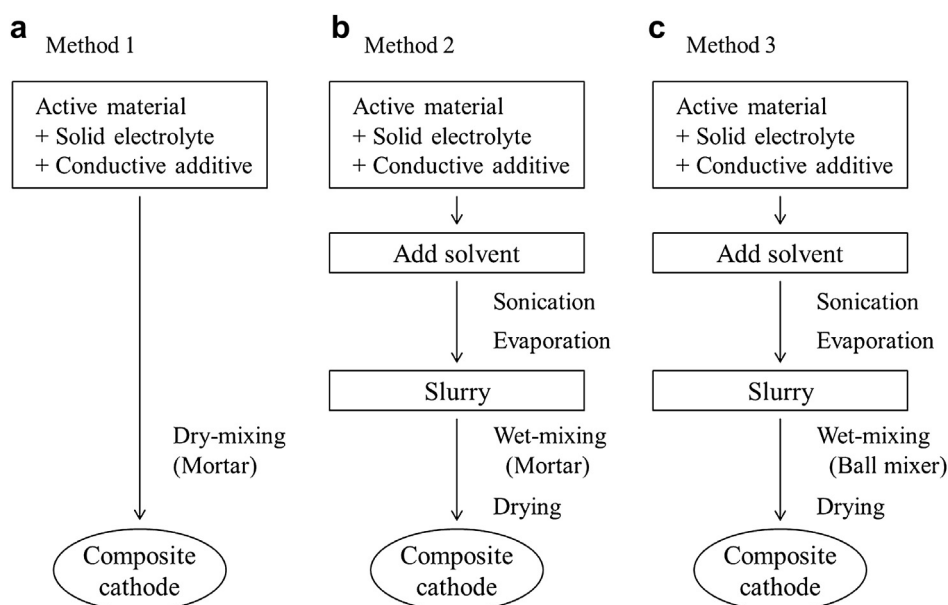


Fig. 1. Schematic diagrams for the three preparation methods of the composite cathode: (a) dry-mixing with hands (method 1), (b) wet-mixing with hands (method 2) and (c) wet-mixing with a ball mixer (method 3).

3. Results and discussion

To compare the effects of the mixing methods on the microstructures of the composite cathodes, the SEM images and the corresponding EDX element (P, Co and C) maps of the composite cathodes were measured for the specimen prepared by different mixing methods as shown in Fig. 2. In all the images in this figure, a common feature is that the blue-colored LiCoO_2 and green-colored Super P carbon particles are dispersed between the red-colored solid electrolyte particles, which have a mashed shape due to the relatively soft nature of the sulfide electrolytes. However, some morphological differences between the composite cathodes prepared by the different mixing methods are observed. For the composite cathode prepared only by dry-mixing with hands (method 1) in Fig. 2(a), large agglomerates of the LiCoO_2 and Super P carbon particles, which are held together by weak and physical van der Waals forces, are seen over a wide region. On the other hand, the agglomeration of Super P carbon particles is greatly alleviated in the composite cathode prepared by sonication and wet-mixing with hands (method 2), even if agglomerates of LiCoO_2 are still observed. This indicates that using dry-mixing only is insufficient to uniformly disperse and mix the Super P carbon nanoparticles.

For the wet-mixing method, a ball mixer rotating at high speed in place of the agate mortar and pestle was used to improve the

dispersion of the constituent particles. In Fig. 2(c), wet-mixing with the ball mixer (method 3) can be seen to disperse the agglomerates of the LiCoO_2 and Super P carbon particles more effectively. Although it is known that it is difficult to mix these particles because the heavier LiCoO_2 particles settle down and the lighter carbon particles tend to float in the slurry preparation step for liquid electrolyte systems [10], in this case, the wet-mixing method is certainly more effective to improve the degree of mixing of all the solid particles as well as to prepare the composite cathode for the all-solid-state battery system. This is because of the better movement of the particles.

Fig. 3 shows the initial charge and discharge curves of the composite cathodes prepared by different mixing methods. Although a large irreversible capacity was found for all the cells during the initial charge, the 1st charge and discharge capacities of the all-solid-state cell using the composite cathode prepared by method 3 reached the highest value of around 139 and 113 mAh g^{-1} at a current density of 0.06 mA cm^{-2} , which is larger than those prepared by method 1 and 2.

The effect of the mixing method for preparing the composite cathodes on the cycling performances (i.e., specific capacity, capacity retention and coulombic efficiency as a function of the cycle number) of the all-solid-state cells is compared in Fig. 4(a)–(c). As expected from the results of Fig. 2, the composite cathode prepared by method 1 shows the lowest charge/discharge capacity

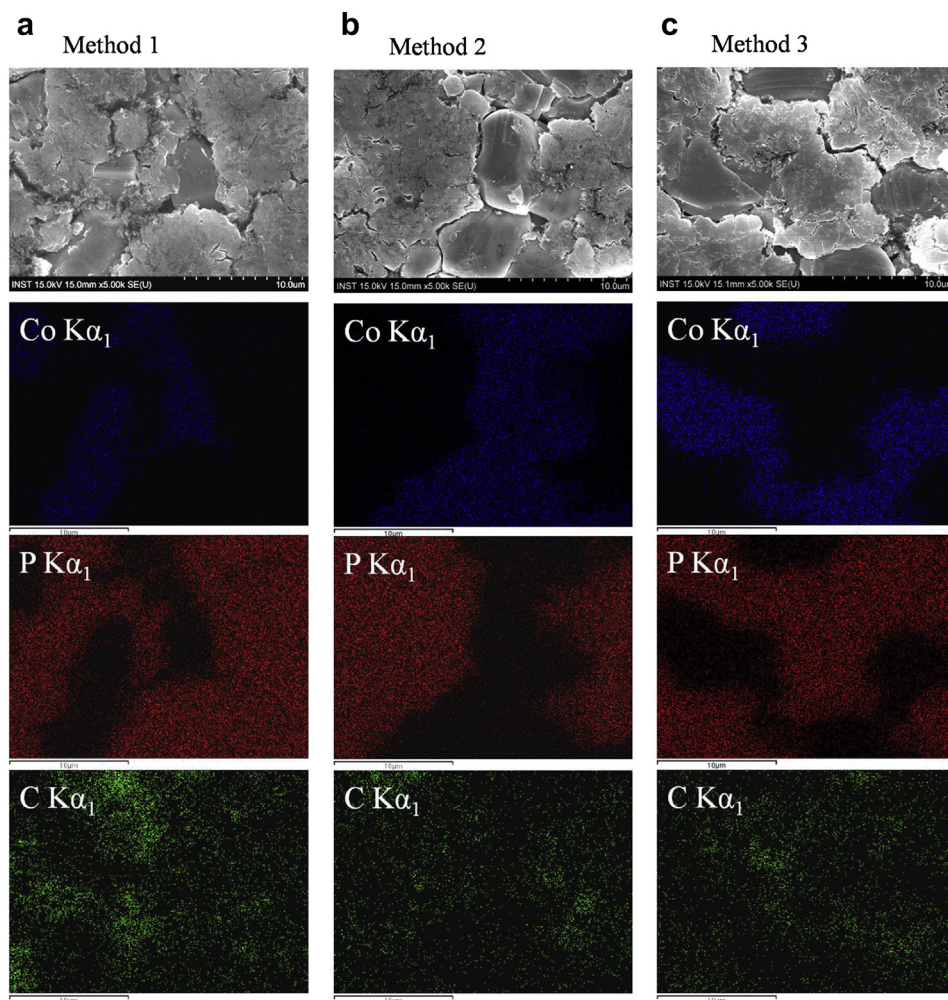


Fig. 2. SEM images and corresponding EDX elements maps of the composite cathodes prepared by (a) dry-mixing with hands (method 1), (b) wet-mixing with hands (method 2) and (c) wet-mixing with a ball mixer (method 3).

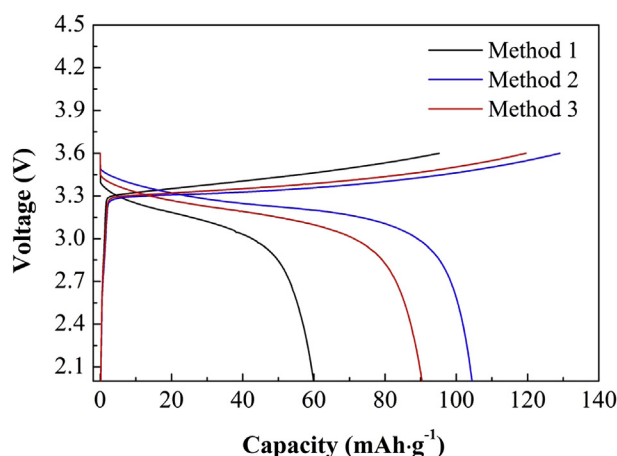


Fig. 3. Charge–discharge curves of the all-solid-state cells using composite cathodes prepared by three different mixing methods.

during all cycles and the lowest coulombic efficiency during initial cycles, while the charge/discharge capacity and coulombic efficiency of the composite cathode prepared by method 2 are improved by the modification of the mixing method from dry to wet due to the substantial decrease of the Super P carbon agglomerates. However, the discharge capacity and coulombic efficiency drastically decline after the 30th cycle despite its higher initial capacity. This results in a low discharge capacity similar to that of the composite cathode prepared by method 1 after the 50th cycle in the end due to the aggregation of the LiCoO_2 particles remaining after the mixing process. On the other hand, the composite cathode prepared by method 3 clearly shows better capacity retention and coulombic efficiency of almost 100% after the 4 cycles as well as larger capacity during all cycles compared with that prepared by method 1 and 2. The discharge capacity of 84 mAh g^{-1} is maintained at the 50th cycle with a capacity retention of 75%, which is larger than 63 and 49% of that observed with the composite cathodes prepared by method 1 and 2, respectively. If the active materials or conductive additives are inhomogeneously distributed, the active materials are not evenly utilized and they also experience unequal topological potential [10]. Then, some of the active materials are overcharged and overdischarged, which eventually degrade their activity and result in gradual capacity fading. Therefore, the remarkably improved cycling performance of the composite cathode prepared by method 3 can be attributed to the more desirable particle distribution of LiCoO_2 as well as the Super P carbon in the composite cathode. This improvement demonstrates that sonication followed by wet-mixing using a ball mixer is an effective way to enhance the cycling performance of the all-solid-state cells.

In an effort to more comprehensively understand the effect of the mixing method for preparing the composite cathodes on the cycling performance of the all-solid-state cells, the AC impedance spectra of the fully charged and discharged all-solid-state cells at the 1st and 10th cycles were analyzed (Fig. 5). It was reported that, in an impedance profile of the all-solid-state cells, the resistance components in the high and low frequency region can be attributed to the resistance of the solid electrolyte and indium negative electrodes, respectively. The semicircle observed in the middle frequency region can be assigned to the charge transfer resistance at the interface between the active materials and the solid electrolyte [11].

In Fig. 5, the common feature is that the interfacial resistance of all the cells using the composite cathode prepared by the different mixing methods increases after the 10th cycle. It has already been

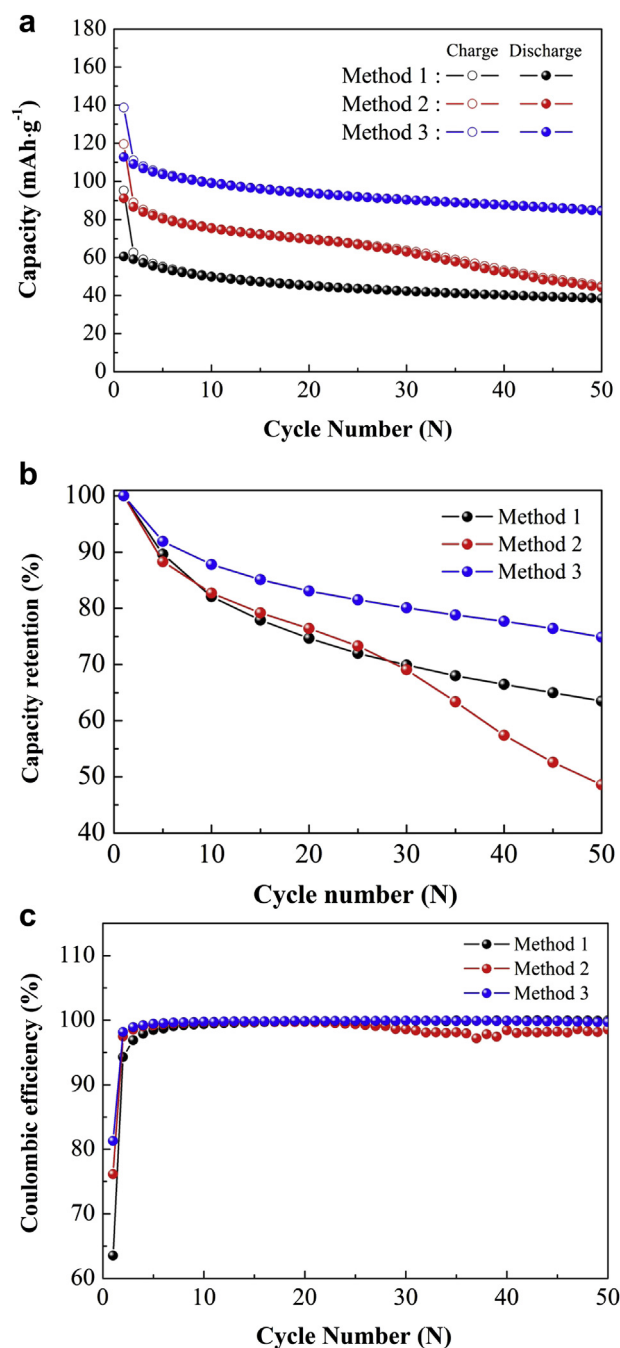


Fig. 4. (a) Specific capacity and (b) discharge capacity retention of the all-solid-state cells using composite cathodes prepared by three different mixing methods as a function of the cycle number.

reported that various surface coating techniques were developed to suppress the increase of the interfacial resistance between the oxide cathode materials and the sulfide solid electrolytes, which is a typical phenomenon originating from one or all three of either a highly developed space-charge layer, diffusion of the active materials, or consumption of the active materials [12–14]. However, since a study of the chemical reaction at the interface between the oxide active materials and the sulfide solid electrolytes is beyond our scope, it will not be discussed here.

In Fig. 5(a), a noticeable feature is that the interfacial resistance of the fully charged all-solid-state cell using the composite cathode prepared by method 3 is substantially reduced at both the 1st and

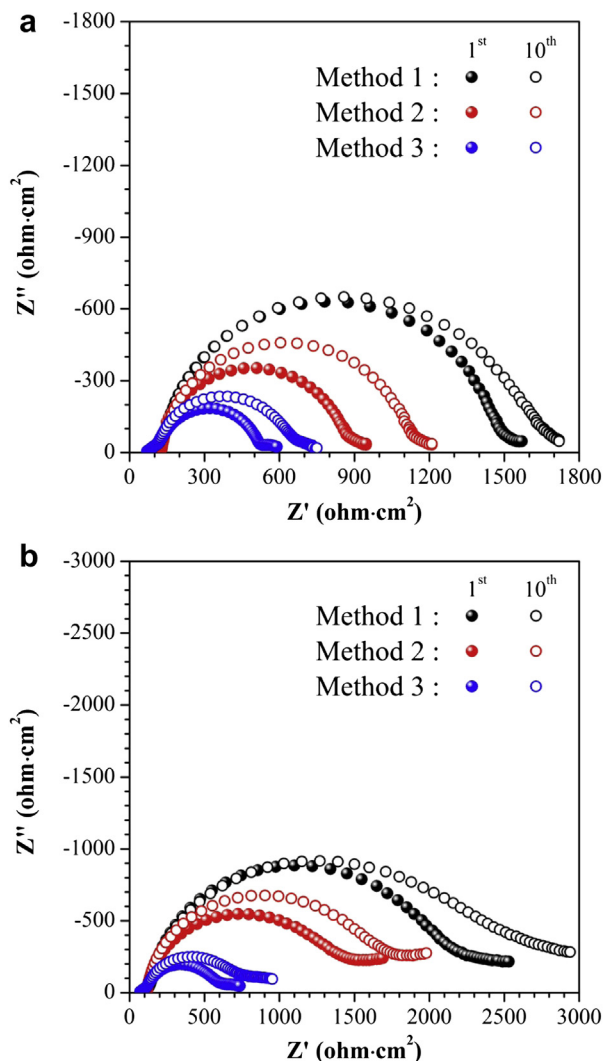


Fig. 5. Variation in the AC impedance spectra (1st → 10th cycles) of the all-solid-state cells using composite cathodes prepared by three different mixing methods after (a) a full charge to 3.6 V and (b) a full discharge to 1.9 V.

10th cycle compared to that prepared by method 1 and 2, even when the interfacial resistance of all the cells increases after the 10th cycle. In addition, a similar variation is observed for the fully discharged cells shown in Fig. 5(b) except that the cell resistance for the discharge is larger than that for charging since the Li^+ insertion into the solid lattices of the active materials is kinetically slower than the Li^+ extraction [15]. The changes of interfacial resistance values by the different mixing methods are summarized in Table 2. This indicates that the better cycling performance of the composite cathode prepared by method 3 is closely related to the decrease in the composite cathode resistance due to the improvement of the

Table 2

Change of interfacial resistance of the fully charged and discharged all-solid-state cells at the 1st and 10th cycles.

Mixing method	Interfacial resistance (Ω) at 1st cycle		Interfacial resistance (Ω) at 10th cycle	
	Charge	Discharge	Charge	Discharge
Method 1	1345.3	1992.2	1497.5	2354.7
Method 2	754.7	1350.2	999.2	1615.1
Method 3	407.1	502.7	558.8	651.2

contact environment between the constituent particles by modification of the mixing method for preparing the composite cathode. In the all-solid-state cells, an electrochemical reaction occurs at the solid–solid interface between the solid electrolytes, electrode materials and conductive additives. Thus, adequate contact between these materials is of greater necessity to facilitate fast lithium ion and electron conduction and achieve good performance of the all-solid-state cells.

In addition to the results of cell impedance, in order to further identify the effect of the mixing method for preparing composite cathodes on the cycling performance of the all-solid-state cells, the variation in the electrode polarization of the charged and discharged cells at the 1st cycle was compared in the differential capacity curves shown in Fig. 6. The shifts and broadening of the major redox peaks were observed in the potential range of 3.1–3.4 V with a change in the mixing method for preparing the composite cathode. The potential difference between the anodic peak and the cathodic peak (ΔV) is known to indicate reversibility of the Li^+ intercalation/deintercalation process on charge–discharge cycling, wherein a larger potential difference represents stronger electrode polarization [16]. A quantitative comparison of Table 1 shows that the electrode polarization is reduced in the composite cathode prepared by method 3 ($\Delta V = 0.083$ V), which demonstrates better reversibility of the charge and discharge cycling. This result can be explained on the basis of the homogeneity of the mixing state. The sonication followed by wet-mixing with the ball mixer provides a more uniform distribution and a more favorable contact environment for LiCoO_2 , solid electrolyte and Super P carbon particles in the composite cathode (Fig. 2), which in turn allows the cell resistance to decrease. As a result, the smaller cell resistance (Fig. 5) leads to smaller electrode polarization (Fig. 6) and eventually to better cycle performance (Fig. 4).

From this work, it is confirmed that the performance of the all-solid-state lithium batteries can be greatly enhanced by modifying

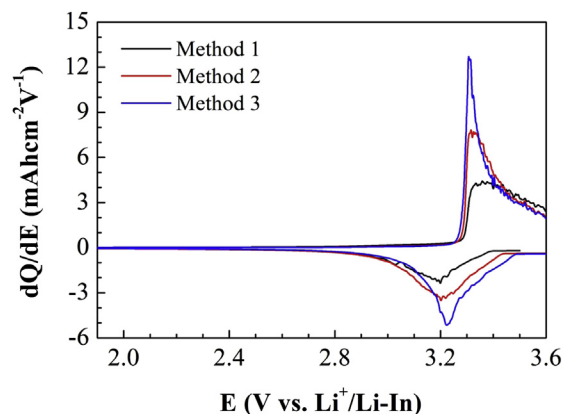


Fig. 6. Differential capacity versus voltage curves of the all-solid-state cells using the composite cathodes prepared by three different mixing methods at the 1st cycle.

Table 1

A quantitative comparison of the potential difference between anodic and cathodic peak potentials for all-solid-state cells using composite cathodes prepared by three different mixing methods.

	Cathodic peak potential (V)	Anodic peak potential (V)	Potential difference (ΔV)
Method 1	3.355	3.198	0.157
Method 2	3.316	3.205	0.111
Method 3	3.307	3.224	0.083

the mixing method for preparing the composite cathode. Although this work does not present an optimized preparation process for the composite cathode, it clearly shows that the preparation process of the composite cathode is critically important in all-solid-state lithium batteries.

4. Conclusions

The distribution of solid particles was compared for composite cathode prepared with three different mixing methods. It was found that even if the same components are used, the morphological properties differ according to the mixing method. The composite cathode prepared by a mixing method consisting of sonication followed by wet-mixing with a ball mixer, shows that all the constituent particles are more uniformly distributed. As a result, favorable particle-to-particle contact leads to lower cell resistance and electrode polarization permitting higher reversible capacity at all cycle numbers. Therefore, development of the most suitable and further optimized mixing process for all-solid-state battery systems is critical to achieve high cell performance.

Acknowledgments

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the

Korean Ministry of Knowledge Economy (grant no. 10037233) and the research fund of Hanyang University (HY-2005-M).

References

- [1] A. Hayashi, K. Minami, M. Tatsumisago, J. Non-cryst. Solids 355 (2009) 1919–1923.
- [2] A. Hayashi, K. Minami, S. Ujiie, M. Tatsumisago, J. Non-cryst. Solids 356 (2010) 2670–2673.
- [3] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, Nat. Mater. 10 (2011) 682–686.
- [4] S. Adams, R. Prasada Rao, J. Mater. Chem. 22 (2012) 7687–7691.
- [5] F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, J. Power Sources 146 (2005) 711–714.
- [6] A. Sakuda, A. Hayashi, M. Tatsumisago, J. Power Sources 195 (2010) 599–603.
- [7] T.A. Yersak, J.E. Trevey, S.H. Lee, J. Power Sources 196 (2011) 9830–9834.
- [8] J. Kim, Y. Yoon, J. Lee, D. Shin, J. Power Sources 196 (2011) 6920–6923.
- [9] J. Kim, M. Eom, S. Noh, D. Shin, Electron. Mater. Lett. 8 (2012) 209–213.
- [10] J.K. Hong, J.H. Lee, S.M. Oh, J. Power Sources 111 (2002) 90–96.
- [11] A. Sakuda, H. Kitora, A. Hayashi, K. Tadanaga, M. Tatsumisago, J. Electrochem. Soc. 156 (2009) A27–A32.
- [12] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, Adv. Mater. 18 (2006) 2226–2229.
- [13] N. Ohta, K. Takada, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada, T. Sasaki, Electrochem. Commun. 9 (2007) 1486–1490.
- [14] A. Sakuda, A. Hayashi, M. Tatsumisago, Chem. Mater. 22 (2010) 949–956.
- [15] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B.N. Popov, J. Power Sources 91 (2000) 122–129.
- [16] Y.Z. Dong, Y.M. Zhao, Y.H. Chen, Z.F. He, Q. Kuang, Mater. Chem. Phys. 115 (2009) 245–250.